



Designation: D5453 – 24

Standard Test Method for Determination of Total Sulfur in Light Hydrocarbons, Spark Ignition Engine Fuel, Diesel Engine Fuel, and Engine Oil by Ultraviolet Fluorescence¹

This standard is issued under the fixed designation D5453; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope*

1.1 This test method covers the determination of total sulfur in liquid hydrocarbons, boiling in the range from approximately 25 °C to 400 °C, with viscosities between approximately 0.2 cSt and 20 cSt (mm²/s) at room temperature.

1.2 Three separate interlaboratory studies (ILS) on precision, and three other investigations that resulted in an ASTM research report, have determined that this test method is applicable to naphthas, distillates, engine oil, ethanol, Fatty Acid Methyl Ester (FAME), and engine fuel such as gasoline, oxygen enriched gasoline (ethanol blends, E-85, M-85, RFG), diesel, biodiesel, diesel/biodiesel blends, and jet fuel. Samples containing 1.0 mg/kg to 8000 mg/kg total sulfur can be analyzed (Note 1).

NOTE 1—Estimates of the pooled limit of quantification (PLOQ) for the precision studies were calculated. Values ranged between less than 1.0 mg/kg and less than 5.0 mg/kg (see Section 10 and 17.1).

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use. For warning statements, see 4.1, 8.3, 8.4, Section 9, and 10.1.*

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

¹ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.03 on Elemental Analysis.

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2. Referenced Documents

2.1 ASTM Standards:²

- D1250 Guide for the Use of the Joint API and ASTM Adjunct for Temperature and Pressure Volume Correction Factors for Generalized Crude Oils, Refined Products, and Lubricating Oils: API MPMS Chapter 11.1
- D1298 Test Method for Density, Relative Density, or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method
- D4052 Test Method for Density, Relative Density, and API Gravity of Liquids by Digital Density Meter
- D4057 Practice for Manual Sampling of Petroleum and Petroleum Products
- D4175 Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants
- D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products
- D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance

3. Terminology

3.1 Definitions:

3.1.1 For definitions of terms used in this test method, refer to Terminology D4175.

4. Summary of Test Method

4.1 A hydrocarbon sample is either directly injected or placed in a sample boat. The sample or boat, or both, is inserted into a high temperature combustion tube where the sulfur is oxidized to sulfur dioxide (SO₂) in an oxygen rich atmosphere. Water produced during the sample combustion is removed and the sample combustion gases are next exposed to ultraviolet (UV) light. The SO₂ absorbs the energy from the UV light and is converted to excited sulfur dioxide (SO₂*). The fluorescence emitted from the excited SO₂* as it returns to a stable state,

² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at www.astm.org/contact. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

*A Summary of Changes section appears at the end of this standard

SO₂, is detected by a photomultiplier tube and the resulting signal is a measure of the sulfur contained in the sample. (**Warning**—Exposure to excessive quantities of ultraviolet (UV) light is injurious to health. The operator must avoid exposing any part of their person, especially their eyes, not only to direct UV light but also to secondary or scattered radiation that is present.)

5. Significance and Use

5.1 Some process catalysts used in petroleum and chemical refining can be poisoned when trace amounts of sulfur bearing materials are contained in the feedstocks. This test method can be used to determine sulfur in process feeds sulfur in finished products, and can also be used for purposes of regulatory control.

6. Interferences

6.1 This test method is applicable for total sulfur determination in liquid hydrocarbons containing less than 0.35 % (m/m) halogen(s).

6.2 *Nitric Oxide (NO) Interference*—When in sufficient concentrations, bound nitrogen compounds present in the test specimen, may cause sulfur results to be biased high for apparatus types that do not account for the potential interference. See [Annex A1](#) for instructions in determining if nitrogen

interference is significant for a given apparatus or sulfur determination application.

7. Apparatus

7.1 *Furnace*—An electric furnace held at a temperature (1050 °C min to 1150 °C max) sufficient to pyrolyze all of the sample and oxidize sulfur to SO₂. The actual temperature to be recommended by the specific apparatus manufacturer.

7.2 *Combustion Tube*—A quartz combustion tube constructed to allow the direct injection of the sample into the heated oxidation zone of the furnace or constructed so that the inlet end of the tube is large enough to accommodate a quartz sample boat. The combustion tube shall have one or more side arms for the introduction of oxygen and carrier gas or air. The oxidation section shall be large enough (see [Fig. 1](#)) to ensure complete combustion of the sample. [Fig. 1](#) depicts conventional combustion tubes. Other configurations are acceptable if precision is not degraded.

7.3 *Flow Control*—The apparatus shall be equipped with a means of flow control that is capable of maintaining a constant supply of oxygen and carrier gas or air.

7.4 *Drier Tube*—The apparatus must be equipped with a mechanism for the removal of water vapor. The oxidation reaction produces water vapor which must be eliminated prior

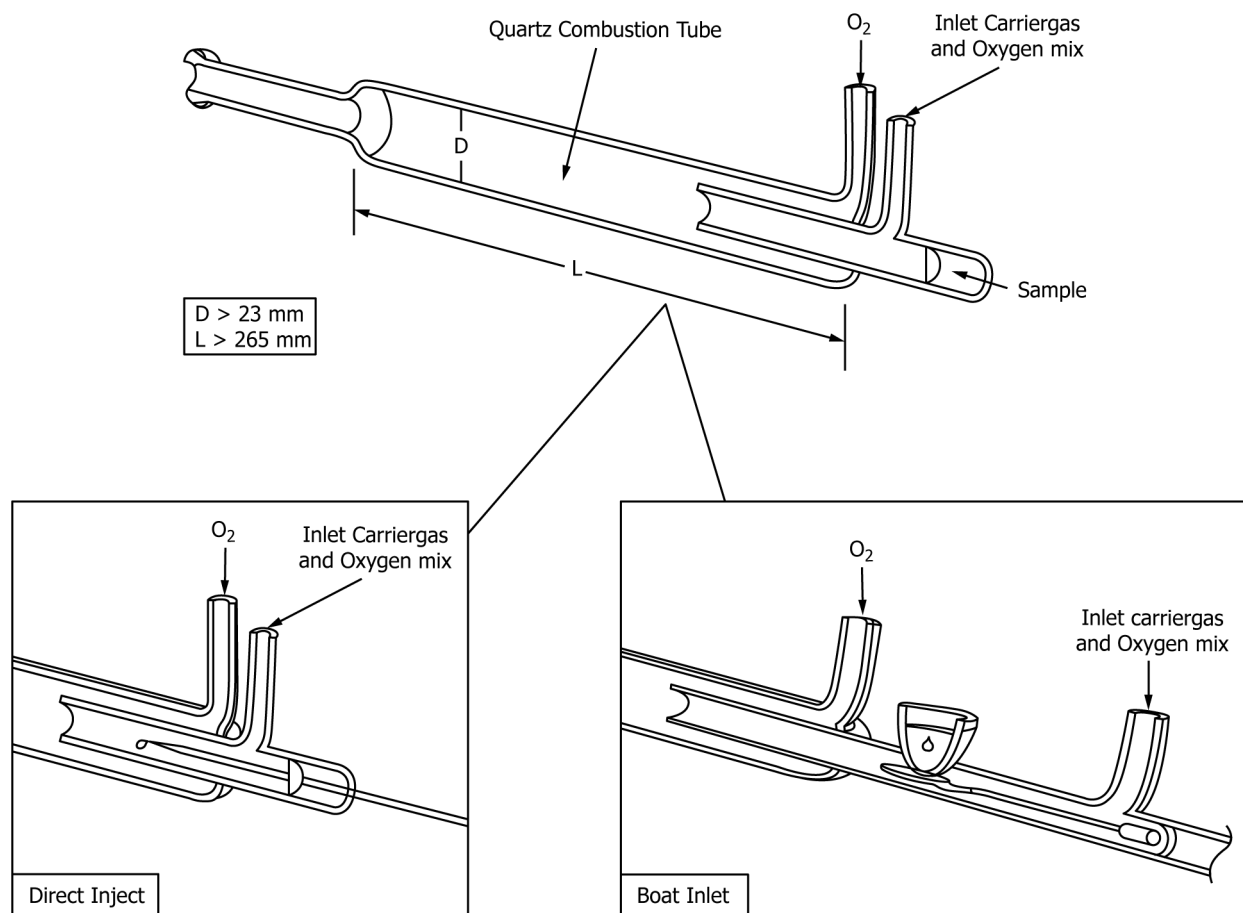


FIG. 1 Conventional Combustion Tubes

to measurement by the detector. This can be accomplished with a membrane drying tube, or a *permeation dryer*, that utilizes a selective capillary action for water removal.

7.5 UV Fluorescence Detector—A qualitative and quantitative detector capable of measuring light emitted from the fluorescence of sulfur dioxide by UV light.

7.6 Microlitre Syringe—Capable of accurately delivering from 5 μL to 90 μL of test specimen. Check with the instrument manufacturer for specific test specimen volume and needle size requirements.

7.7 Sample Inlet System—Either of two types of sample inlet systems can be used.

7.7.1 Direct Injection—A direct injection inlet system must be capable of allowing the quantitative delivery of the material to be analyzed into an inlet carrier stream which directs the sample into the oxidation zone at a controlled and repeatable rate. A syringe drive mechanism which discharges the sample from the microlitre syringe at a rate of approximately 1 $\mu\text{L/s}$ is typical. Check with the instrument manufacturer for specific test specimen injection rates. For example, see Fig. 2.

7.7.2 Boat Inlet System—An extended combustion tube provides a seal to the inlet of the oxidation area and is swept by a carrier gas. The system provides an area to position the sample carrying mechanism (boat) at a retracted position removed from the furnace. The boat drive mechanism will fully insert the boat into the hottest section of the furnace inlet. The sample boats and combustion tube are constructed of quartz. The combustion tube provides a cooling jacket for the area in which the retracted boat rests awaiting sample intro-

duction from a microlitre syringe. A drive mechanism which advances and withdraws the sample boat into and out of the furnace at a controlled and repeatable rate is required. For example, see Fig. 3.

7.8 Refrigerated Circulator—An adjustable apparatus capable of delivering a coolant material at a constant temperature as low as 4 $^{\circ}\text{C}$ could be required when using the boat inlet injection method (optional).

7.9 Strip Chart Recorder, (optional).

7.10 Balance, with a precision of ± 0.01 mg (optional).

8. Reagents

8.1 Purity of Reagents—Reagent grade chemicals shall be used in tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.³ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 Carrier Gas—Inert gas or air. The actual gas to be recommended by the specific apparatus manufacturer.

³ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopoeial Convention, Inc. (USPC), Rockville, MD.

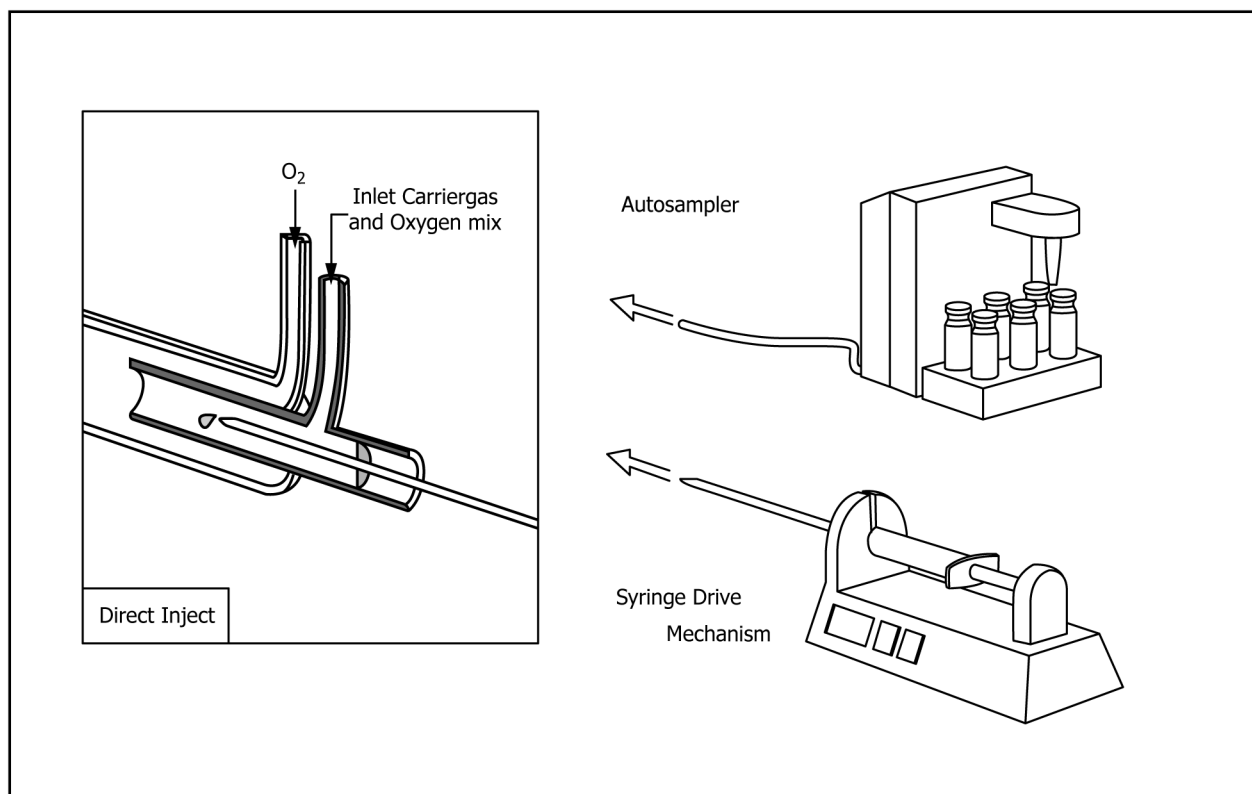


FIG. 2 Direct Inject Syringe Drive

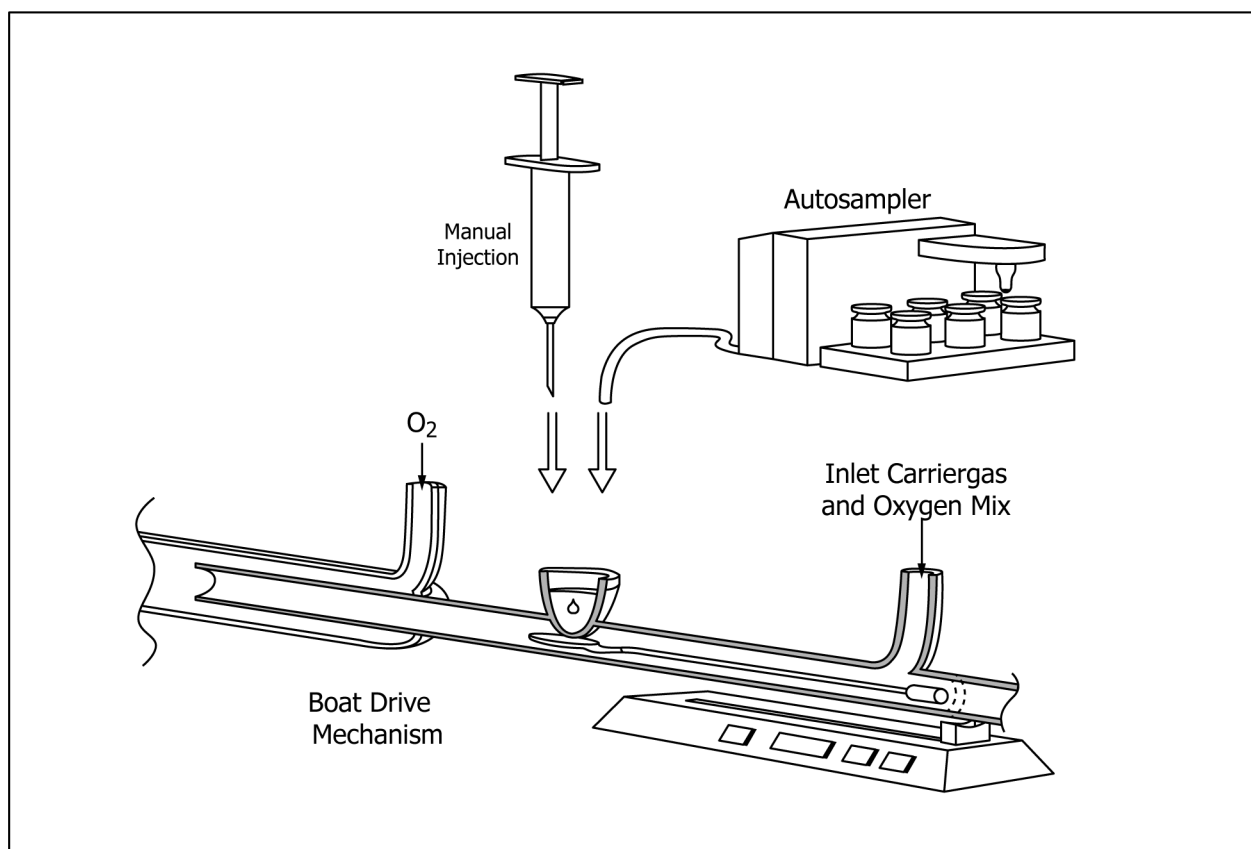


FIG. 3 Boat Inlet System

8.2.1 *Inert Gas*—Argon or helium only, high purity grade (that is, chromatography or zero grade), 99.998 % minimum purity, moisture 5 mg/kg maximum.

8.2.2 *Air*—High purity grade (that is, chromatography or zero grade), 99.99 % minimum purity, moisture 5 mg/kg maximum.

8.3 *Oxygen (as required)*—High purity (that is, chromatography or zero grade), 99.75 % minimum purity, moisture 5 ppm w/w maximum, dried over molecular sieves. (**Warning**—Vigorously accelerates combustion.)

8.4 *Toluene, Xylenes, Isooctane*, reagent grade (other solvents similar to those occurring in samples to be analyzed are also acceptable). Correction for sulfur contribution from solvents (solvent blank) used in standard preparation and sample specimen dilution is required. Alternatively, use of a solvent with nondetectable level of sulfur contamination relative to the sulphur content in the sample unknown makes the blank correction unnecessary. (**Warning**—Flammable solvents.)

8.5 *Dibenzothiophene*, FW184.26, 17.399 % (m/m) S (Note 2).

8.6 *Butyl Sulfide*, FW146.29, 21.92 % (m/m) S (Note 2).

8.7 *Thionaphthene (Benzothiophene)*, FW134.20, 23.90 % (m/m) S (Note 2).

NOTE 2—A correction for chemical impurity can be required.

8.8 *Quartz Wool*, or other suitable absorbent material that is stable and capable of withstanding temperatures inside the furnace (see Note 3).

NOTE 3—Materials meeting the requirements in 8.8 provide a more uniform injection of the sample into the boat by wicking any remaining drops of the sample from the tip of the syringe needle prior to introduction of the sample into the furnace. Consult instrument manufacturer recommendations for further guidance.

8.9 *Sulfur Stock Solution*, 1000 µg S/mL—Prepare a stock solution by accurately weighing approximately 0.5748 g of dibenzothiophene or 0.4562 g of butyl sulfide or 0.4184 g of thionaphthene into a tared 100 mL volumetric flask. Dilute to volume with selected solvent. This stock can be further diluted to desired sulfur concentration (Notes 4-7).

NOTE 4—Working standards that simulate or match the composition or matrix of the samples analyzed can reduce test result bias between direct inject and boat sample inlet systems.

NOTE 5—Working standards should be remixed on a regular basis depending upon frequency of use and age. Typically, stock solutions have a useful life of about three months.

NOTE 6—Calibration standards can be prepared and diluted on a mass/mass basis when result calculations are adjusted to accommodate them.

NOTE 7—Calibration standards from commercial sources can be used if checked for accuracy and if precision is not degraded.

8.10 *Quality Control (QC) Samples*, preferably are portions of one or more liquid petroleum materials that are similar to